



# CHORUS

This is the accepted manuscript made available via CHORUS. The article has been published as:

## Homes scaling in ionic liquid gated $\text{La}_{\{2\}}\text{CuO}_{\{4+x\}}$ thin films

J. Kinney, J. Garcia-Barriocanal, and A. M. Goldman

Phys. Rev. B **92**, 100505 — Published 21 September 2015

DOI: [10.1103/PhysRevB.92.100505](https://doi.org/10.1103/PhysRevB.92.100505)

# Homes Scaling in Ionic Liquid Gated $\text{La}_2\text{CuO}_{4+x}$ Thin Films

J. Kinney, J. Garcia-Barriocanal, and A. M. Goldman

*School of Physics and Astronomy, University of Minnesota,  
116 Church Street SE, Minneapolis, Minnesota 55455, USA*

(Dated: September 1, 2015)

Finding more efficient ways of exploring the doping phase diagrams of high temperature superconductors as well as probing the fundamental properties of these materials are essential ingredients for driving the discovery of new materials. We use a doping technique involving gating with ionic liquids to systematically and continuously tune the  $T_c$  of superconducting  $\text{La}_2\text{CuO}_{4+x}$  thin films. We probe both the transport properties and the penetration depth of these samples and find that Homes scaling  $\lambda^{-2} \propto \sigma T_c$  is obeyed, consistent with these materials being in the dirty limit. This result is independent of the precise mechanism for the gating process as all of the parameters of the scaling relationship are determined by direct measurements on the films.

The study of high-temperature superconductivity is a field dating back to the discovery of  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ .<sup>1</sup> Since that time, there has been a steady drive to increase the transition temperature of these materials with the ultimate goal of finding a room temperature superconductor which could unlock many practical technologies. At a basic level this push for higher transition temperatures is a material search. Ionic liquids offer the exciting possibility of increasing the efficiency of this search, allowing one to explore a whole range of doping for a material system in a single sample, where previously a whole series of sample growths would be required. We demonstrate the use of ionic liquids in an electric double layer transistor configuration to continuously tune the transition temperature of superconducting  $\text{La}_2\text{CuO}_{4+x}$  (LCO) thin films. This allows us to precisely monitor how the change in the carrier concentration affects the transition temperature, resistance and superconducting penetration depth of the material. We highlight these details and demonstrate through the verification of Homes scaling<sup>2</sup> that that this approach is nevertheless a powerful alternative to chemical doping for systematically studying the properties of high-temperature superconductors. This is true despite the fact that the doping in this material may not be a purely electrostatic effect.

These films were grown by ozone-assisted molecular beam epitaxy.<sup>3</sup> We use Cu and La Knudsen effusion cells to produce stable rates for these two materials. The rate for each source is measured prior to the film growth using a quartz crystal microbalance. We alternately deposit one half of a unit cell of La then Cu by opening shutters for each source. The film presented here is 3 unit cells thick. The substrate temperature is 700 °C as measured by a Williamson Pro 92-38 pyrometer and under an ozone pressure of  $3 \times 10^{-5}$  torr during growth. We monitor the growth of the films using RHEED and see strong 2D film streaks epitaxially locked to the  $a$  and  $b$  axes of the substrate's lattice. We use  $\langle 001 \rangle$  oriented  $\text{SrLaAlO}_4$  substrates supplied by MTI corp. The  $T_c$  of the initial sample before the application of ionic liquid and gate voltage is well-defined and is greater than 40K, which is a sign of high quality and implies that the excess oxygen is near its maximal value of  $x=0.12$ .

Tuning the properties of high  $T_c$  materials using a conventional FET configuration is a well established technique for systematically adjusting the carrier concentration of superconducting materials.<sup>4-6</sup> The use of ionic liquids to tune the properties of thin films has grown rapidly in the past several years due to the possibility of producing large changes in the carrier concentration of a material. Some of the first efforts in this regard were by Iwasa's group.<sup>7</sup> In terms of studying high temperature superconductors, this technique has been applied to  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ,<sup>8</sup>  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ,<sup>9,10</sup> LCO<sup>11</sup> and  $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ .<sup>12</sup> In all of these studies the focus was on the superconductor-insulator transition. The work presented here is an extension of that done on LCO with the technique of penetration depth measurements added in parallel with standard transport measurements. This combination allows us to determine the evolution of the relationships between various superconducting and normal state properties with applied gate voltage and temperature.

We used a two-coil mutual inductance technique for tracking the penetration depth.<sup>6,13-17</sup> The experimental setup is shown in Fig. 1. Both the drive and pickup coils are located on the back side of the sample. The holder is constructed out of Delrin. We use an SRS SR830 lock-in amplifier to both produce the drive signal and in conjunction with an SRS SR560 amplifier to measure the output from the pickup coil. The AC drive signal has a frequency of 50 kHz and an amplitude of 1 mA. We use a numerical procedure for determining the penetration depth of the sample from the measured real and imaginary components of the voltage read by the pickup coil. We model the film with a complex impedance,  $Z = R + i\omega L_k$ , where  $R$  and  $L_k$  are the sheet resistance and the kinetic inductance of the film, respectively. In the case of a thin film with thickness  $d$  and  $\lambda \gg d$ , the kinetic inductance is directly related to the London penetration depth as  $L_k = \mu_0 \lambda^2 / d$ , where  $\mu_0$  is the permeability of free space and  $\lambda$  is the London penetration depth.

We used the ionic liquid DEME-TFSI to tune the properties of our superconducting samples. The ionic liquid is initially applied to the surface of the sample at room temperature but all further gating is done at 245 K. Figure

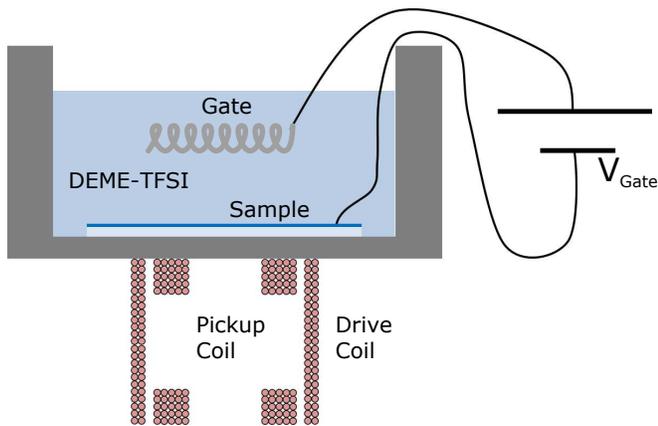


FIG. 1. (color online) Schematic of the sample setup. The entire sample is immersed in the ionic liquid DEME-TFSI. A gate electrode made of Pt is also immersed in the ionic liquid. Not pictured are leads going to the corners of the sample for making resistance measurements. The sample holder is made of plastic (Delrin) to minimize extraneous screening currents. The two-coil assembly is composed of an outer drive coil and an inner pickup coil. The inner pickup coil consists of two oppositely wound sections to minimize the direct mutual inductance between the drive coil and the pickup coil. The sample is patterned into a disk with a 5 mm diameter. The inner diameters of the pickup coil and drive coil are 2 mm and 3 mm respectively. The gate is a coil of Pt wire with a surface area double that of the sample.

2 shows how the resistance, carrier concentration, and mobility evolve with the applied gate voltage at a temperature of 180K. All three quantities were determined using a 4-wire resistance technique in a van der Pauw configuration. Each measurement step involves warming the sample and ionic liquid to 245 K, which is above the melting point of the liquid. The gate voltage is then changed at this elevated temperature and allowed to relax for 20 min. We apply a positive voltage to the gate, which corresponds to removing holes or reducing the number of charge carriers in the sample. As the gate voltage is increased we see both an increase in the resistance of the film and a decrease in the carrier concentration. While the mobility does begin to decrease at higher gate voltages we see that the primary effect of the applied voltage is to reduce the number of free holes in the material. We note that the gating procedure is not purely electrostatic as the changes upon gating are irreversible. The evidence for this conclusion comes from removing the applied gate voltage and observing that the resistance does not return to the zero-voltage state. In fact, we must apply a negative gate voltage in order to return the resistance to its initial state. There is evidence in many other material systems doped with ionic liquids showing that the gating process is often a mixture of electrochemical and electrostatic effects.<sup>18–21</sup> Particular to LCO, there is evidence that the interstitial oxygens are mobile down to 200 K<sup>22,23</sup> and it would not be surprising to think that the ionic liquid gating procedure removing holes actually

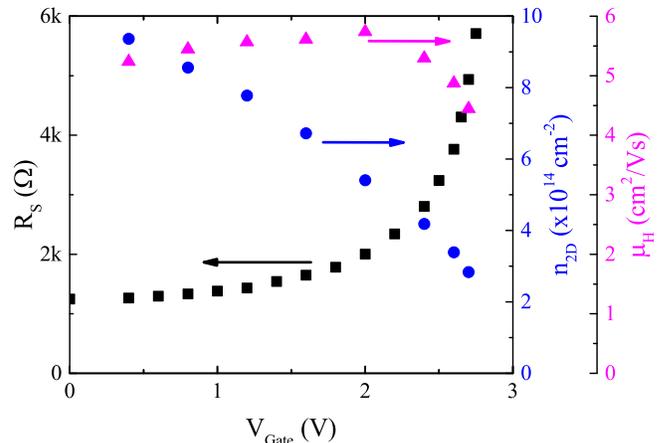


FIG. 2. (color online) Plot showing how  $R_S$  (squares),  $n_{2D}$  (circles), and  $\mu_H$  (triangles) evolve as the gate voltage is increased. All three quantities were measured at 180 K. We see that as we increase the gate voltage the resistance steadily increases and the number of free carriers decreases. We also note that, while the mobility does begin to decrease above 2.5 V, we are primarily affecting the carrier concentration of the film and for the most part the mobility is remaining constant.

removed some oxygen. Now, while there are advantages to a purely electrostatic process, namely reversibility and no introduction of disorder, an *in-situ* electrochemical doping method, which we believe may be involved in the process presented here, is still a powerful and useful tool.

Due to imprecise knowledge of the distance between the coils and the sample, we cannot determine the absolute size of the penetration depth. Instead, to set the scale, we use 2700 Å based on literature values for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ <sup>24–26</sup> a compound with a similar transition temperature, to calibrate the unknown spacing between the sample and the coils. We then measure changes in the penetration depth from that starting point as we adjust the doping of the sample using the gate electrode in the ionic liquid. The real and imaginary components of the voltage in the pickup coil are shown in Fig. 3. The real component has a peak centered at the superconducting transition and the width of the peak is, in part, a measure of the homogeneity of the sample at that doping. We see that with increasing applied gate voltage the peak moves to lower temperatures and broadens. We interpret this as a change in the doping of the material, removing holes, but not necessarily in a fully homogeneous way. We will use the center of this peak as our definition of  $T_c$  for the purposes of checking the Homes scaling relation.<sup>2</sup> The imaginary component of the voltage, while not explicitly equal to it, represents the kinetic inductance of the sample which is directly related to both the penetration depth and superconducting electron density. We see that the imaginary component moves to lower temperatures and goes to zero with increasing gate

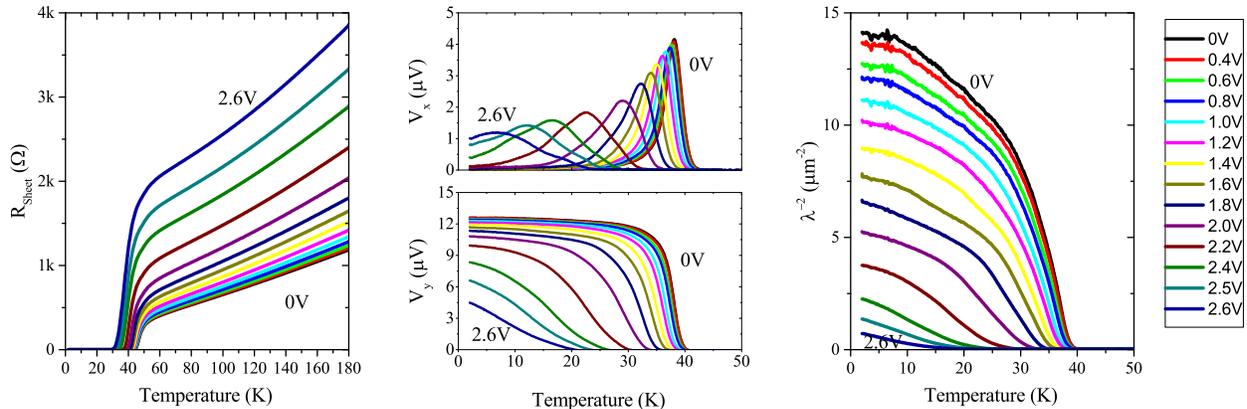


FIG. 3. (color online) (Left) The sheet resistance of a 3 unit cell LCO sample tuned using ionic liquids. The initial, 0V, state has the highest  $T_c$  and the lowest resistance. As the gate voltage is increased  $T_c$  decreases and the normal state resistance increases. (Center) The real and imaginary components of the voltage in the pickup coil. The real component,  $V_x$ , is peaked at  $T_c$  of the film and becomes broader with increasing gate voltage. The imaginary component,  $V_y$ , is maximal at the lowest temperature and decreases with increasing gate voltage. (Right) The inverse of the London penetration depth squared, which is proportional to the superconducting electron density, grows with decreasing temperature below  $T_c$ .

voltage. Data on the resistance of the sample can be obtained in parallel with the two-coil signal. We see that as we increase the gate voltage and remove holes the normal state resistance increases and  $T_c$  steadily decreases. We can translate the combination of real and imaginary components of the pickup coil signal into the penetration depth of the sample.

The first thing to check is the temperature dependence of the penetration depth. Depending on the pairing state of the superconductor we expect  $\Delta\lambda$  to have a specific temperature dependence. For an  $s$ -wave pairing state with a full gap we expect an exponential dependence for  $\Delta\lambda$ . For a  $d$ -wave pairing state, where there are nodes in the gap, we expect a linear dependence for  $\Delta\lambda$ . In the case of strong scattering this linear dependence shifts to  $\Delta\lambda \propto T^2$ .<sup>27</sup> We have seen (not shown) that this sample exhibits a quadratic temperature dependence, which implies scattering is playing a significant role. The ultra thin nature of this sample means that the upper and lower surface roughness make up a large fraction of the thickness of the entire film. We used both X-ray reflectivity (XRR) and atomic force microscopy (AFM) to characterize the film roughness. From fitting the XRR using GenX we estimate the substrate-sample interface RMS roughness and the sample surface RMS roughness are 3 Å and 8 Å, respectively. Using AFM we measure the sample surface RMS roughness to be 3 Å measured over a 1 μm square area. All of these quantities are significant compared to the  $c$ -axis lattice parameter, which is 13.3 Å. Considering that the entire film thickness is 3 unit cells and the roughness of both of the top and bottom surface are significant fractions of a unit cell it is reasonable to expect this film to be in the strong scattering limit.

The next check that we can make with this data set is to see if the Homes scaling relationship is obeyed.<sup>2,28</sup> Fig-

ure 5 demonstrates that  $\lambda^{-2} \propto T_c\sigma$  does in fact provide a good description of our data. We use the conductivity at 180 K and define  $T_c$  using the peak value of the real component of the two-coil signal. Both of these are clearly defined values even when the transition becomes broad at higher gate voltages. The scaling relationship also holds when the conductivity just at the onset of superconductivity is employed. Following the work of Zuev *et al.*<sup>29</sup> we can use the relationship

$$k_B T_{2D} = \frac{\Phi_0^2}{8\pi\mu_0} \frac{d}{\lambda^2(T_{2D})}, \quad (1)$$

to define  $T_{2D}$ , which is the Berezinskii-Kosterlitz-Thouless-transition temperature. Here  $\Phi_0$  is the flux quantum. If we use the entire film thickness of 40 Å as the value of  $d$  we find good agreement between this definition of  $T_{2D}$  and the value of  $T_c$  that we determine from the peak of the real component of the two coil signal.

There are a number of different proposals for the interpretation of the  $\lambda^{-2} \propto \sigma T_c$  relationship.<sup>30-33</sup> The simplest argument comes from the fact that the film is in the strong scattering limit ( $\Delta \ll \hbar\tau^{-1}$ ) to begin with. For our films we use a simple Drude model to estimate the scattering rate. Taking the values of  $R_s$  and  $n_{2D}$  from Fig. 2 and the relationship  $\frac{1}{R_s} = \frac{n_{2D}e^2\tau}{m}$  we can calculate  $\hbar\tau^{-1}$  to be 1.3 eV, which is much larger than the superconducting gap in these types of materials.<sup>34</sup> It is important to note that while the Homes data set is a compilation of many samples measured over the course of many years, the data shown here is from a single sample continuously doped to cover a range of  $T_c$  values in a systematic and efficient manner. This points to the power of using ionic liquids in an electric double layer transistor configuration to systematically study the fun-

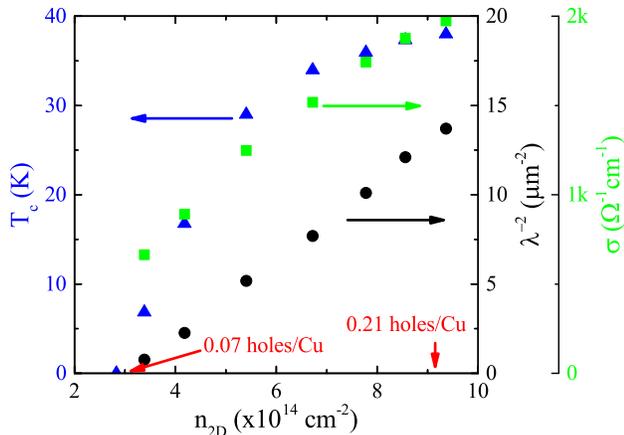


FIG. 4. (color online) Plot showing how  $T_c$  (triangles),  $\lambda(0)^{-2}$  (circles), and  $\sigma$  (squares) evolve as a function of doping in a 3 unit cell LCO thin film. Conductivity data is taken at 180 K. For reference we include markers at the top and the underdoped edge of the superconducting dome, where the conversion from charges per square cm to holes per copper is done using the fact that we have a 3 unit cell sample which corresponds to 6 copper oxygen planes.

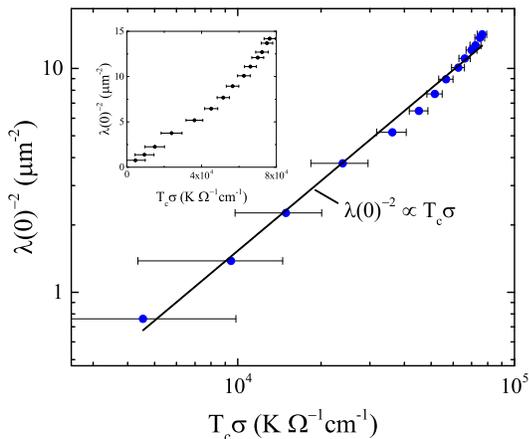


FIG. 5. (color online)  $\lambda(0)^{-2}$  vs  $T_c\sigma$  for a 3 unit cell LCO film. The inset shows the same data on a linear scale. The properties of the film were systematically tuned using the ionic liquid and gate electrode setup pictured in Fig. 1. We see a linear relationship between  $\lambda(0)^{-2}$  and  $T_c\sigma$  in agreement with the scaling relationship seen by Homes *et al.*

fundamental properties of superconducting samples.

The initial motivation for exploring whether there is a fundamental relationship between  $T_c$  and  $\lambda^{-2}$  was derived from the empirical relationship proposed by Uemura *et al.*<sup>35</sup> The data presented here does not follow

the relationship proposed by Uemura of  $T_c \propto \lambda^{-2}$ . This is actually readily seen by a more careful examination of Fig. 4. We see that the quantity  $\lambda^{-2}$ , which is proportional to the superconducting electron density, increases linearly with the number of free carriers in the normal state. Simply, the number of superconducting carriers in the superconducting state is proportional to the number of free holes in the normal state. This means that we could simply switch the x-axis of Fig. 4 from doping (carrier concentration) to  $\lambda^{-2}$  without effecting the shape of the  $T_c$  curve. This means the relationship between  $T_c$  and  $\lambda^{-2}$  will just be a remapping of the superconducting dome and therefore not a linear function as seen by Uemura in other, chemically doped high- $T_c$  materials. There is precedent for a sub-linear relationship for  $T_c \propto [\lambda^{-2}]^x$ , where a value of  $x = 0.5$  follows from an argument about critical scaling where there is a quantum critical point (QCP) at the edge of the dome.<sup>26,29</sup> While we do see a sub-linear relationship ( $x < 1$ ), it is not a pure single power law over the range of dopings examined here, much of which is likely far from the QCP point.

In summary, we have used the ionic liquid DEME-TFSI to systematically tune the transition temperature of under-doped LCO thin films, and have displayed and analyzed data from a 3-unit cell thick film. This has allowed us to carefully track how the resistance, Hall Effect, and penetration depth are interrelated. Our results are in good agreement with the Homes scaling relation consistent with the fact that this film is in the strong scattering limit. In addition, this unique setup allows us to explicitly show that the super-electron density, as measured by  $\lambda^{-2}$ , is linearly proportional to the free carriers in the normal state. As a result of this linear dependence we see that any fundamental relationship between  $T_c$  and  $\lambda^{-2}$  will just be a remapping of the superconducting dome. These results are independent of the precise mechanism associated with the doping process, which may in part be electrochemical, rather than purely electrostatic. This suggests that ionic liquid gating may be a powerful way to explore the phase diagram of other materials, and should be considered to be an effective complement to conventional chemical doping.

The authors would like to thank Rafael Fernandes and Peter Orth for useful discussions. This work was primarily supported by the National Science Foundation through the University of Minnesota MRSEC under Award Number DMR-1420013 and partially supported by the National Science Foundation under Award Number DMR-1209578. Part of this work was carried out at the University of Minnesota Characterization Facility, a member of the NSF-funded Materials Research Facilities Network via the MRSEC program, and the Nanofabrication Center which receives partial support from the NSF through the NNIN program.

- 
- <sup>1</sup> J. G. Bednorz and K. A. Müller, *Zeitschrift für Physik B Condensed Matter* **64**, 189 (1986).
- <sup>2</sup> C. C. Homes, S. V. Dordevic, M. Strongin, D. A. Bonn, R. Liang, W. N. Hardy, S. Komiya, Y. Ando, G. Yu, N. Kaneko, X. Zhao, M. Greven, D. N. Basov, and T. Timusk, *Nature* **430**, 539 (2004).
- <sup>3</sup> D. D. Berkley, B. R. Johnson, N. Anand, K. M. Beauchamp, L. E. Conroy, A. M. Goldman, J. Maps, K. Mauersberger, M. L. Mecartney, J. Morton, M. Tuominen, and Y.-J. Zhang, *Applied Physics Letters* **53**, 1973 (1988).
- <sup>4</sup> D. Matthey, N. Reyren, J.-M. Triscone, and T. Schneider, *Physical Review Letters* **98**, 057002 (2007).
- <sup>5</sup> M. Salluzzo, A. Gambardella, G. M. De Luca, R. Di Capua, Z. Ristic, and R. Vaglio, *Physical Review B* **78**, 054524 (2008).
- <sup>6</sup> A. Rüfenacht, J.-P. P. Locquet, J. Fompeyrine, D. Caimi, and P. Martinoli, *Physical Review Letters* **96**, 227002 (2006).
- <sup>7</sup> K. Ueno, S. Nakamura, H. Shimotani, A. Ohtomo, N. Kimura, T. Nojima, H. Aoki, Y. Iwasa, and M. Kawasaki, *Nature materials* **7**, 855 (2008).
- <sup>8</sup> A. T. Bollinger, G. Dubuis, J. Yoon, D. Pavuna, J. Misewich, and I. Božović, *Nature* **472**, 458 (2011).
- <sup>9</sup> X. Leng, J. Garcia-Barriocanal, S. Bose, Y. Lee, and A. M. Goldman, *Physical Review Letters* **107**, 027001 (2011).
- <sup>10</sup> X. Leng, J. Garcia-Barriocanal, B. Yang, Y. Lee, J. Kinney, and A. M. Goldman, *Physical Review Letters* **108**, 067004 (2012).
- <sup>11</sup> J. Garcia-Barriocanal, A. Kobrinskii, X. Leng, J. Kinney, B. Yang, S. Snyder, and A. Goldman, *Physical Review B* **87**, 024509 (2013).
- <sup>12</sup> S. W. Zeng, Z. Huang, W. M. Lv, N. N. Bao, K. Gopinadhan, L. K. Jian, T. S. Heng, Z. Q. Liu, Y. L. Zhao, C. J. Li, H. J. Harsan Ma, P. Yang, J. Ding, T. Venkatesan, and Ariando, *Physical Review B* **92**, 020503 (2015).
- <sup>13</sup> A. Hebard and A. Fiory, *Physical Review Letters* **44**, 291 (1980).
- <sup>14</sup> B. Jeanneret, J. L. Gavilano, G. A. Racine, C. Leemann, and P. Martinoli, *Applied Physics Letters* **55**, 2336 (1989).
- <sup>15</sup> Z.-H. Lin, G. C. Spalding, A. M. Goldman, B. F. Bayman, and O. T. Valls, *Europhysics Letters (EPL)* **32**, 573 (1995).
- <sup>16</sup> S. J. Turneaure, E. R. Ulm, and T. R. Lemberger, *Journal of Applied Physics* **79**, 4221 (1996).
- <sup>17</sup> S. J. Turneaure, A. a. Pesetski, and T. R. Lemberger, *Journal of Applied Physics* **83**, 4334 (1998).
- <sup>18</sup> J. Jeong, N. Aetukuri, T. Graf, T. D. Schladt, M. G. Samant, and S. S. P. Parkin, *Science (New York, N.Y.)* **339**, 1402 (2013).
- <sup>19</sup> J. Jeong, N. B. Aetukuri, D. Passarello, S. D. Conradson, M. G. Samant, and S. S. P. Parkin, *Proceedings of the National Academy of Sciences* **112**, 1013 (2015).
- <sup>20</sup> A. C. Lang, J. D. Sloppy, H. Ghassemi, R. C. Devlin, R. J. Sichel-Tissot, J.-C. Idrobo, S. J. May, and M. L. Taheri, *ACS Applied Materials and Interfaces* **6**, 17018 (2014).
- <sup>21</sup> T. A. Petach, M. Lee, R. C. Davis, A. Mehta, and D. Goldhaber-Gordon, *Physical Review B* **90**, 081108(R) (2014).
- <sup>22</sup> M. Fratini, N. Poccia, A. Ricci, G. Campi, M. Burghammer, G. Aeppli, and A. Bianconi, *Nature* **466**, 841 (2010).
- <sup>23</sup> X. Xiong, P. Wochner, S. C. Moss, Y. Cao, K. Koga, and M. Fujita, *Physical Review Letters* **76**, 2997 (1996).
- <sup>24</sup> T. Startseva, T. Timusk, A. V. Puchkov, D. N. Basov, H. A. Mook, M. Okuya, T. Kimura, and K. Kishio, *Physical Review B* **59**, 8 (1998).
- <sup>25</sup> G. Aeppli, E. J. Ansaldo, J. H. Brewer, R. J. Cava, R. F. Kiefl, S. R. Kreitzman, G. M. Luke, and D. R. Noakes, *Physical Review B* **35**, 7129 (1987).
- <sup>26</sup> T. R. Lemberger, I. Hetel, A. Tsukada, M. Naito, and M. Randeria, *Physical Review B* **83**, 140507 (2011).
- <sup>27</sup> M. Prohammer and J. P. Carbotte, *Physical Review B* **43**, 5370 (1991).
- <sup>28</sup> C. C. Homes, S. V. Dordevic, T. Valla, and M. Strongin, *Physical Review B* **72**, 134517 (2005).
- <sup>29</sup> Y. Zuev, M. Seog Kim, and T. R. Lemberger, *Physical Review Letters* **95**, 137002 (2005).
- <sup>30</sup> Y. Imry, M. Strongin, and C. C. Homes, *Physical Review Letters* **109**, 067003 (2012).
- <sup>31</sup> V. G. Kogan, *Physical Review B* **87**, 220507 (2013).
- <sup>32</sup> B. J. Taylor and M. B. Maple, *Physical Review B* **76**, 184512 (2007).
- <sup>33</sup> D. N. Basov and A. V. Chubukov, *Nature Physics* **7**, 272 (2011).
- <sup>34</sup> M. Hashimoto, I. M. Vishik, R.-H. He, T. P. Devereaux, and Z.-X. Shen, *Nature Physics* **10**, 483 (2014).
- <sup>35</sup> Y. Uemura, G. Luke, B. Sternlieb, J. Brewer, J. Carolan, W. Hardy, R. Kadono, J. Kempton, R. Kiefl, S. Kreitzman, P. Mulhern, T. Riseman, D. Williams, B. Yang, S. Uchida, H. Takagi, J. Gopalakrishnan, A. Sleight, M. Subramanian, C. Chien, M. Cieplak, G. Xiao, V. Lee, B. Statt, C. Stronach, W. Kossler, and X. Yu, *Physical Review Letters* **62**, 2317 (1989).